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The interface of a model polymer composite has been probed using solid-state NMR techniques. The adsorption of aminoalkylsilane coupling agents onto silica surfaces and the interaction of these functional silanes with a bismaleimide resin was studied. Carbon-13 CP/MAS NMR was used to confirm the bonding between the silane and bismaleimide (BMI) resin and elucidate the nature of the crosslinking reaction of BMI. Deuterated coupling agents were synthesized, adsorbed, and reacted on silica surfaces. The deuterium labels on the coupling agents allowed their dynamics to be probed independently of the other organic materials present through the use of ^{2}H solid-echo NMR. The experimental results were consistent with motions where the alkyl portion of the coupling agent undergoes gauche migration (gtt ↔ ttg) and pair gauche production (ttt ↔ gtg) conformational isomerizations plus slow anisotropic rotation. The room temperature spectra were simulated with a model that included hopping between two discrete sites on the tetrahedral lattice with a jump rate of $8x10^{5}$ sec^{-1} and plus rotational diffucional constants of $R_{\parallel}=7x10^{4}$ sec^{-1} and $R_{\perp}=1x10^{4}$ sec^{-1}. Polymerizing BMI resin over the chemisorbed coupling agent resulted in a line shape that could be modelled as a simple two site jump with occupational probabilities of 0.7 and 0.3 and a jump frequency of $1.7x10^{5}$ sec^{-1}. The anisotropic rotation was no longer required to simulate these spectra. The types of motions of the coupling agent were not affected significantly over the temperature range-100 °C to 85°C, although the exchange rate was changed.

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Molecular Mobility of the Interface in a Model Composite: A NMR Study

by

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Abstract

The interface of a model polymer composite has been probed using solid-state NMR techniques. The adsorption of aminoalkylsilane coupling agents onto silica surfaces and the interaction of these functional silanes with a bismaleimide resin was studied. Carbon-13 CP/MAS NMR was used to confirm the bonding between the silane and bismaleimide (BMI) resin and elucidate the nature of the crosslinking reaction of BMI. Deuterated coupling agents were synthesized, adsorbed, and reacted on silica surfaces. The deuterium labels on the coupling agents allowed their dynamics to be probed independently of the other organic materials present through the use of ^2H solid-echo NMR. The experimental results were consistent with motions where the alkyl portion of the coupling agent undergoes gauche migration (gtt ↔ ttg) and pair gauche production (ttt ↔ gtg) conformational isomerizations plus slow anisotropic rotation. The room temperature spectra were simulated with a model that included hopping between two discrete sites on the tetrahedral lattice with a jump rate of 8×10^5 sec^{-1} and plus rotational diffusional constants of $R_{\parallel} = 7 \times 10^4$ sec^{-1} and $R_{\perp} = 1 \times 10^4$ sec^{-1}. Polymerizing BMI resin over the chemisorbed coupling agent resulted in a line shape that could be modelled as a simple two site jump with occupational probabilities of 0.7 and 0.3 and a jump frequency of 1.7×10^5 sec^{-1}. The anisotropic rotation was no longer required to simulate these spectra. The types of motions of the coupling agent were not affected significantly over the temperature range -100 °C to 85 °C, although the exchange rate was changed.

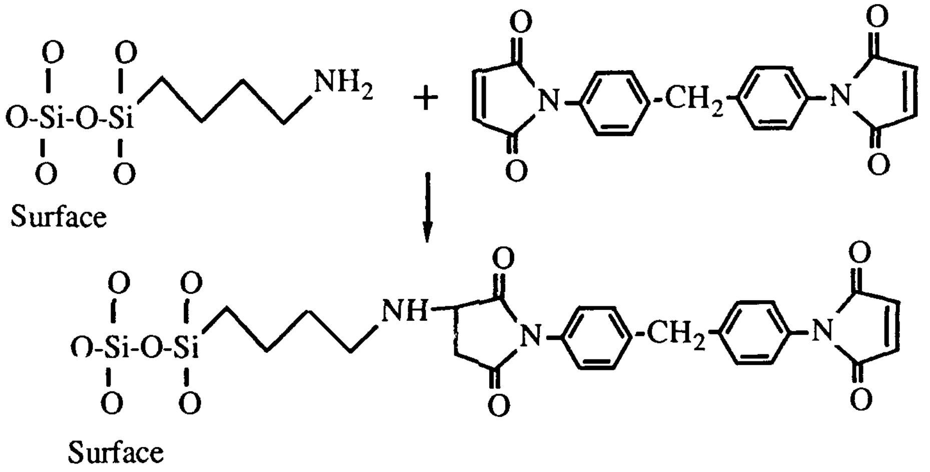
Introduction

Reinforced polymer composites often consist of two major components: an inorganic phase such as glass fibers and an organic polymer matrix. The function of the polymer matrix is to bind the fibers together, transfer the load to the fibers, and protect them from environmental factors.[1] The properties of composites are influenced by the properties of the constituents and the interactions among them. Various bismaleimide resins are polymers currently in use in the aerospace industry for composite materials of construction in aircraft and space vehicles.[2] Bismaleimides have physical characteristics somewhere between epoxies and other polyimides. They are easily processed like epoxy resins and have long-term stability up to 200-230 °C.

The fiber/polymer interface plays a crucial role in the performance of the composite. The bond between the matrix and the fiber has to effectively transfer the load from the polymer to the reinforcing fibers. A weak interface may result in the failure of the composite. Strong interfacial bonding is also important for transverse strength and resistance to environmental factors. Silane coupling agents are often used to improve the adhesion between the two constituents in a polymer composite. They have been the subject of broad application and study because of their ability to covalently bond organic and inorganic materials.[3] The presence of trace quantities of coupling agents in polymer composites can greatly enhance performance, particularly in the presence of moisture which is responsible for many composite failures.

A significant amount of work has been done using FTIR, carbon-13 and silicon-29 NMR spectroscopy to characterize silane coupling agents,[4-24] in addition to other techniques. The majority of these studies have focused on the structure of the coupling agents at or near the surface. Sindorf and Maciel[10] have observed differences in the mobility of aliphatic silanes which increase in mobility with chain length. Ho *et al.*[17] have used ^{29}Si cross-polarization times to study the relative mobilities of certain silane species under different condition. However, lack of precise distance information makes quantization of their data in terms of molecular motion difficult. Another approach which can be used to probe the dynamics of molecules at the interface is wide-line deuterium NMR. Specific labelling with deuterium provides a site specific, non-perturbing probe for molecular motion. The analysis of the resultant line shapes can yield a model for the type and frequency of molecular motion. The ^2H NMR technique has been used to study the molecular motions of silanes chemisorbed on silica,[25-32] but not in the presence of a polymer matrix. Through the use of a specifically labelled coupling agent it is possible to directly probe the interface in the presence of a polymer overlayer. The ^2H NMR technique is novel because the sample does not need to be optically transparent nor are clean surfaces and high vacuum techniques required. Alternately, carbon-13 labelling can be used,[33] but the results have not been very quantitative in terms of the mechanism or rate of molecular motion.

In this study, we have chemisorbed deuterium labelled amino-functional silane coupling agents onto silica through a condensation reaction. This reaction forms siloxane linkages (Si-O-Si) between the coupling agent and silica. The amino functionality of the coupling agent is then covalently bonded to the polymer matrix, in this case bismaleimide (BMI). Schematically the reaction between the coupling agent and BMI is represented by:



The structure of reacted coupling agent and BMI was determined through solid-state carbon-13 cross-polarization magic-angle spinning NMR and comparison with the results of a model reaction between methylmaleimide and butylamine. The molecular motion of the coupling agents was investigated using deuterium NMR at various temperatures. Simulated line shapes which matched the experimental spectra were used to suggest possible motions of the coupling agent in the presence of the polymer.

Experimental Section

Sample Preparation.

Model Reaction. *N*-methylmaleimide (Aldrich) and n-butylamine (Fisher) were used as received. The reaction was conducted in two different solvents, acetone and toluene. N-methylmaleimide was dissolved in acetone and reacted with butylamine by refluxing in acetone at 55 °C for 90 minutes. Acetone was rotary evaporated and a thick copper-brown liquid recovered. This product was analyzed without separation by ^1H and ^{13}C NMR to be 2-(*N*'-butylamino)-*N*-methylmaleimide. The reaction in acetone yielded the major product as well as a small amount of a by-product which was not characterized. The reaction in toluene was carried out at 60 °C and resulted in the formation of a single product, 2-(*N*'-butylamino)-*N*-methylmaleimide.

Curing of Bismaleimide. The bismaleimide resin, 1,1'-(methylenedi-4,1-phenylene)bismaleimide (BMI), was obtained from Aldrich and used as received. Curing reactions were carried out in a crucible by heating at 185 °C for times ranging from 15 minutes to 4 hours. The cured resins were ground into powder and analyzed using ^{13}C CP-MAS.

Bismaleimide and Silane Coupling Agents. The coupling agents, aminopropyltrimethoxysilane (APMS), aminopropyltriethoxysilane (APES), and aminobutyltriethoxysilane (ABES), were used as received from Aldrich, after analysis by NMR to determine that they were not hydrolyzed to any measurable extent. (Once hydrolyzed, the coupling agents are referred to as APS and ABS.)

APMS and BMI were reacted in 2-butanone by heating at 80 °C for 90 minutes.[34] The product of this reaction was a white insoluble precipitate. The reaction of APES and BMI was conducted in the same manner, however, no precipitate formed and the product was a brown viscous solution. This solution was rotary evaporated to remove the solvent. The reaction of ABES and BMI also resulted in a brown sticky product that was rotary evaporated and then put in a vacuum oven at 60 °C for 24 hours. This step resulted in polymerizing the product into a clear, yellow, glassy polymer. The above reactions were not conducted in toluene because BMI is not soluble in it.

The reactions of the surface bound coupling agents (APS and ABS) and BMI were conducted in a similar manner. BMI was first dissolved in 2-butanone and the silica (treated with coupling agent as described below) added in an amount calculated to correspond to approximately stoichiometric equivalence.

Deuterated coupling agents were synthesized via the method previously described.[28,35] About 15 grams of 2-cyanoethyl-(or propyl-)triethoxysilane (Aldrich) was reacted with deuterium gas in a glass reactor. Raney nickel (Aldrich) was used as the catalyst. The reaction was heated to 85 °C and deuterium gas (Linde) charged into the system to 95 psi. The system was recharged with deuterium gas 10-15 times during the first 30 minutes and several times over the next 5 hours. The reaction was allowed to proceed another 12 hours without recharging. The product was vacuum distilled at 30 mm Hg and 85 °C. It was analyzed by FTIR, ^{13}C and ^{2}H NMR. About a 50% yield of purified product was obtained.

Adsorption of Silane Coupling Agents onto Silica. Fused silica (Cab-O-Sil grade S-17, nominal surface area 400 m^2/g, primary particle size 7 nm) was donated by Cabot Corporation and dried a minimum of two days at 110 °C prior to use. The deposition of the coupling agent was conducted according to the procedure developed by Meesiri.[28, 30] A 2.0% by weight solution of the deuterated coupling agent was hydrolyzed in acetone/distilled water (10/1) for 3.5 hours. A 7 ml aliquot of this solution was then added to 0.15 g of the silica in a 15 ml centrifuge tube. The tube was shaken on a vortex mixer for 1 minute, tumbled at a rate of 20 RPM for 15 minutes and centrifuged at 2000 RPM for 45 minutes. The treated silica was washed twice with distilled water to remove loosely held siloxanes and then dried in a vacuum oven at 90 °C for 12 hours. It was determined earlier that these concentrations of coupling agents would correspond to approximately monolayer coverage or slightly below.[28-30]

NMR Studies.

A Varian VXR-200 NMR spectrometer was used for all the solid-state experiments. For ^{13}C at 50.3 MHz, the spectra were obtained using dipolar decoupling, cross polarization, and magic angle spinning (CP-DD-MAS) techniques. The chemical shifts were externally referenced to hexamethylbenzene. Magic angle spinning rates of *ca.* 3 kHz were used and spinning sidebands eliminated with the TOSS technique.[36] The proton dephased (PDP) ^{13}C CP/MAS spectra were taken with the pulse sequence developed by Opella and Frey.[37] A brief delay without proton decoupling is inserted between development of the ^{13}C magnetization and data acquisition (during which full proton decoupling is used). This delay in the TOSS sequence, during which the high power decoupler is gated off, results in suppression of the protonated carbons due to dipole-dipole interactions.

The deuterium wide-line experiments were done at 30.7 MHz using a quadrupole echo pulse sequence. The typical 90° pulse length was 2 μsec and the repetition time about 0.5 sec. The quadrupole echo pulse sequence used $[180^\circ$ (alternate pulses) - delay - $90_x{}^\circ$ - τ_1- $90_y{}^\circ$ - τ_2 - echo$]_n$ contains a 180° prepulse to reduce coherent noise and acoustic ringing. The spectra of the chemisorbed coupling agents were taken with 30 000 - 40 000 scans for adequate signal to noise. This was necessary because of the dilution effect of the silica.[38] Solution ^{13}C NMR spectra were obtained on a JEOL FX-100 at 25 MHz in $CDCl_3$.

Line shape simulations were performed with two FORTRAN programs. The first was written by D. J. Schneider[39] and is based on the theory developed by Freed[40] for slow-motional electron spin resonance. The program has been modified by us to calculate deuterium line shapes[41] for Brownian and jump diffusion, or a combination of both. The second program is based on models for discrete jumps between sites and was developed by Wittebort, Olejniczak and Griffin.[42] The program calculates the chemical exchange spectra for powders assuming that an echo sequence is used for detecting the signal. Corrections are made for finite pulse width and distortions arising from the delay time between pulses.

Results

Model Reaction. N-methylmaleimide and n-butylamine were reacted in nearly a one to one ratio molar (1.03:1.00). This reaction was conducted in order to characterize the amine *N*-alkylmaleimide reaction, a simplified version of the reaction done by Varma *et al.*[34] The carbon-13 NMR spectra shown in Figure 1, indicate that the double bond of the maleimide reacts with the amino group in a nucleophilic addition reaction to form 2-(*N*'-butylamino)-*N*-methylmaleimide. Resonances were assigned for the methylmaleimide (Figure 1A), butylamine (Figure 1B) and the product (Figure 1C) based on structure-shift correlations[43] and are listed in Table I. The butylamine carbons, *1*, *2* and *3*, are slightly deshielded upon reaction with methylmaleimide. The carbon adjacent to the amine group, *4*, shifts the most from 40.7 ppm to 47.0 ppm. In the methylmaleimide spectrum the resonance due to the carbonyl carbon, at 170.7 ppm, is shifted in the product spectrum to 177.4 and 174.8 (carbons *7* and *8*). The intensity of the resonance due to the ring double bond (134.1 ppm) is reduced significantly. The small remaining intensity is due to a slight excess of methylmaleimide which remained unreacted or incompletely reacted. The new resonances that are present in the spectrum of the product are at 55.7 and 31.4 ppm, and are attributed to the reacting of the ring double bond to form carbons *5* and *6*, respectively.

<Table I> <Figure 1>

Composite Reaction. Various reactions were carried out between BMI and aminoalkyl coupling agents in order to verify actual bond formation. In these reactions, the product was insoluble in all common solvents, suggesting that polymerization had occurred. In order to more fully characterize the reaction products, the curing of BMI was first studied. The ^{13}C NMR spectrum of BMI dissolved in chloroform and the solid state CP/MAS ^{13}C NMR spectra of the monomer and cured BMI were taken (not shown). Table II lists the chemical shift assignments which for BMI are based on the work of Fry and Lind.[44-45] With the curing of BMI, several differences are seen in the spectrum. The carbonyl resonance, *6*, is shifted from 170 ppm to 176 ppm, similar to the model reaction. There is still an appreciable amount of intensity at 170 ppm due to unreacted double bonds adjacent to the carbonyls from BMI. The aliphatic resonance at 39 ppm for the unreacted resin is broadened asymmetrically with curing. Curing of BMI produces a ring methine group resonance at *ca.* 46 ppm for *7'* which is quite broad and not completely resolved.

ble II>

The ^{13}C spectrum of cured BMI does not change much with extent of curing. After 2 hours cure time the amount of carbonyls reacted is essentially unchanged. Lind and Fry[44,45] followed this crosslinking reaction with CP/MAS and estimated the degree of crosslinking by measuring the relative intensity of the carbonyl resonances of reacted versus unreacted BMI. The fraction of maleimide rings that reacted after 2 hours at 220 °C was calculated to be 0.5. After 65 hours of curing the fraction was only 0.8. Additional heating did not increase the amount of reacted rings because of the rigid nature of the highly crosslinked polymer.

The ^{13}C CP/MAS spectrum of the BMI-APMS adduct is shown in Figure 2A and the chemical shift assignments listed in Table III. The product shown is from the reaction of 0.005 mole BMI and 0.003 mole APMS. The loss of the maleimide double bond is unable to be discerned because of the overlapping resonances in the 125 to 135 ppm region. In the spectrum of Figure 2A there is a resonance assigned to *7'*, the ring methine carbon at 34.5 ppm.[44] This resonance is well separated from any resolved resonances from either the cured or uncured BMI, or aminopropylsilane[7]--suggestive of a reaction between BMI and the coupling agent. The BMI methylene, *1*, the ring methine carbon, *8'*, and the methylene next to the nitrogen of the coupling agent, *a*, are expected to be in the 43-50 ppm range from the model reaction and previous work.[44] We believe that these may be assigned as *1* (43 ppm), *8'* (45 ppm) and *a* (48 ppm), but this is a complicated region firm assignments have not been made.

In Figure 2B, the spectrum is shown of the product of BMI and ABES, reacted in a ratio of nearly one to one. The ethoxy carbons are very intense and narrow probably due to their extreme mobility. In this spectrum, the resonance from *7'* now overlaps with that from carbon *b* of the coupling agent at around 34 ppm. Again, tentatively, resonances from *1* (41.8 ppm), a (45.6 ppm), and *8'* are again in the same region although they appear to be sharper than in the APMS material. Figure 2C shows the proton dephased (PDP) spectrum of the BMI-ABES product. In a PDP spectrum only those resonances of carbons with no attached protons or significant mobility are not dephased by static dipolar interactions. Therefore, the resonances from the ethoxy group, e and f, also appear. Carbons 1, 3, 4, 7 and 7' of BMI do not appear in this spectrum since they have an attached proton (as well as do all of the carbons of the coupling agent).

<Figure 2>

Deuterium Solid Echo Experiments. The APES and ABES coupling agents were specifically labelled with deuterium on the amino group and the carbon next to the amine. When the coupling agents are hydrolyzed, the amino-deuterons exchange with water, leaving the last carbon deuterated or $(CH_3CH_2O)_3SiOCH_2(CH_2)_nCD_2NH_2$ with n = 1 or 2.[28]

The ^2H NMR spectra of DABS on silica, DABS on silica with BMI reacted over it, and extra BMI polymerized over that sample are shown in Figure 3. The line shape of the chemisorbed DABS, Figure 3A, has a full width at half height of 75 kHz. The reaction of BMI over the coupling agent results in a line shape for the chemisorbed coupling agent that has a width near the base of 120 kHz and full width at half height of 113 kHz. When extra BMI is overpolymerized, Figure 3C, the resultant spectrum is relatively unchanged. The addition of *extra* BMI and further curing does not appear to affect the motions of the molecules at the interface. This would indicate that the slight excess of the original BMI reacted with all DABS available for reaction. Additional layers of BMI do not appear to increase the rigidity of the interface. The broad feature in the spectrum from about +200 kHz to -200 kHz is due to some probe ringing, plus the possibility of some outer wings of a broader powder component. Because of the ringing and low intensity relative to the noise, it was not possible to properly characterize this component.

ig. 3>

The wide-line spectrum of the deuterated aminobutylsilane chemisorbed on silica with approximately a monolayer coverage was determined for DABS adsorbed on silica by three different preparations (not shown). The first sample was prepared from DABES with 3 1/2 hours hydrolysis in a 10/1 acetone-water mixture. This spectrum had a width at half height of *ca.* 70 kHz. The second sample was prepared by hydrolyzing DABES in 100% water for 3 1/2 hours, and the third sample was hydrolyzed for 1/2 hour in water before being adsorbed onto silica. The width at half height of the spectra of the second and third spectra was approximately 65 kHz and all three line shapes have a width at the base of ca. 120 kHz. The spectra prepared by slightly different methods yielded essentially the same line shape, ± 5 kHz width at half height, suggesting a similar deposition of coupling agent on the silica surface. This level of coverage is approximately a monolayer or slightly below.[29,30] Much longer hydrolysis times, or use of the methyl ester yields spectra consistent with slightly more material on the surface.

Shown in Figure 4 are the temperature dependent spectra of DABS chemisorbed on silica along with simulated spectra. At room temperature and above, the line shapes were modelled using a two site jump about an axis tilted at 54.75° from the magnetic field (the bisector of the tetrahedral) and includes a contribution from slow anisotropic Brownian diffusion.[40] At room temperature the motion about the main axis is faster ($R_{||} = 7 \times 10^4$ sec^{-1}) than the motion about the perpendicular axis ($R_{\perp} = 1 \times 10^4$ sec^{-1}), where $R_{||}$ and $R_{\perp}$ are the parallel and perpendicular components of the rotational diffusion tensor. The spectra of the chemisorbed DABS change very little as the temperature is raised from 20 °C to 85 °C (within experimental error). The simulated spectrum at room temperature was calculated using a jump frequency of 8×10^5 sec^{-1}. This gave the experimentally determined width at half height of 75 kHz. The spectra at 45 and 60 °C (not shown) had widths very similar to the spectrum at 85 °C (70 kHz) and can be modelled using the same rotational parameters plus an increased jump rate of 1×10^6 sec^{-1}. From previous work we estimate the uncertainty of the diffusion and jump rates to be less than a factor of 2.[30] These line shapes are approaching the fast exchange limit where changes in line shapes become insensitive to changes in rates of motion.

4>

At 5 °C a jump frequency of 6×10^5 sec^{-1} was used for the calculated spectrum. The spectra below 0 °C could not be modelled by including a contribution due to rotation or with equal probabilities of jump sites. The low temperature, -100 °C and -60 °C, line shapes shown in Figure 4 look very similar to the line shape of chemisorbed DABS reacted to BMI (Figure 3B). The spectra were simulated with the method of Wittebort *et al.*[42] using a two-site jump model hopping between unequally populated sites (0.7 : 0.3) on the tetrahedral lattice. At -60 °C a jump rate of 4.0×10^5 sec^{-1} was used and at -100 °C the jump rate was 2.7×10^5 sec^{-1}. The spectra of DABS chemisorbed on a silica surface are very similar for different τ values. At very short delays, the experimental spectra show more acoustic ringing. The line shapes are basically unchanged by the waiting period between pulses and therefore should be similar to the Bloch decay line shapes.

In Figure 5 the experimental and simulated room temperature spectra of BMI over chemisorbed DABS as a function of τ, the delay between pulses, are shown. There is a distortion in the spectra as τ increases - the filled in center of the spectra is lost. There is also a loss of signal intensity as evidenced by the increased signal-to-noise at the larger τ values. (The intensity of the spectra have been adjusted to the same vertical scale.) The reductions in intensity were consistent with that expected, although S/N considerations did not allow detailed comparisons. This distortion in line shape is indicative of motions which occur in the intermediate regime. The line shapes were simulated using a model for a two-site hop on the diamond lattice with different occupational probabilities. This type of motion is referred to as a restricted isomerization, because only two of the four possible orientations for a C-D bond vector are populated significantly. The spectra of BMI over chemisorbed DABS were calculated assuming the C-D bond to be jumping between two diamond lattice sites, having an angular separation of 109.5°. The occupational probability was 0.7 to 0.3 and the jump frequency was 1.7 x 10^5 sec^{-1}. The τ dependence of the line shape is described reasonably well by the model as shown in the figure. We note that due to the lack of sensitivity, it was not possible to obtain experimental line shape which show the detail exhibited by the simulated ones.

<Fig. 5>

The results of variable temperature studies on DABS with BMI reacted over it are summarized in Figure 6. The temperature dependence of the line shape is minimal over the range -100 °C to 85 °C. Basically, there is only a small narrowing of the top portion of the spectra as temperature is increased. This corresponds to a slight increase in jump frequency, from 1.0 x 10^5 sec^{-1} to 4.0 x 10^5 sec^{-1}. These motions appear to have a relatively small apparent energy of activation or the motions are actually more complicated because of a distribution of jump rates or other motional complications. The line shapes of Figures 5 and 6 were all fit using the same model with an occupational probability of 0.70 to 0.30. Varying these probabilities to 0.80 : 0.20 or 0.60 : 0.40 did not provide as good a fit taking into account the τ distortions and temperature dependence. Therefore, we estimate the uncertainty of this ratio to be less than ± 10%.

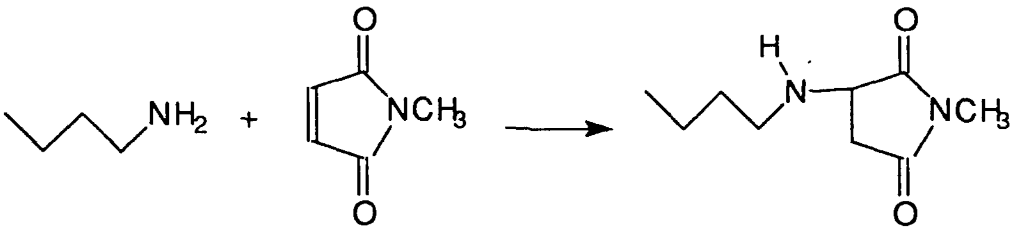
<Fig. 6>

Finally, when the amount of BMI reacted is less than the stoichiometric amount different spectra are obtained (Figure 7). These spectra have been obtained from material with less than an equimolar quantity of BMI reacted over the chemisorbed DABS. Contributions from the reacted DABS (with BMI) and the unreacted DABS are each present, leading to a two-component spectra. As a function of τ, the component due to the BMI-DABS changes with the longer τ values in much the same way as in Figure 5. The component due to unreacted DABS does not change much with τ. These spectra provide a clear distinction of the motional changes that occur upon overpolymerization of the coupling agent with bismaleimide. They also suggest that the reaction with BMI restricts the DABS locally as a broader component is superimposed on the original spectrum with reaction.

<Fig.7>

Discussion

The model reaction between *N*-methylmaleimide and *n*-butylamine resulted in the formation of 2-(*N'*-butylamino)-*N*-methylmaleimide. The reaction proceeded as follows:



It was a very efficient reaction and resulted in the formation of no by-products. This reaction indicates that the amino group acts as a nucleophile adding to the highly electron deficient double bond of the maleimide group. The composite reaction proceeded in a similar manner.

Our previous studies suggest that given the concentrations and amounts of coupling agent and silica, the coupling agent is adsorbed in near monolayer coverage.[29,30] Subsequent heating of the sample facilities Si-O-Surface bond formation.[18-22,30] Based on the adsorption isotherms measured[30] and molecular modelling results, it seems unlikely that there is enough room available for many of the amine groups to directly hydrogen bond to the silica, therefore, we conclude that the coupling agents are "vertical" on average. This is in agreement with photoacoustic infra-red results.[46] However, there still is enough molecular motion to partially average the quadrupole power pattern. It was not possible to model the motions of the chemisorbed DABS, at room temperature, as a simple two site hop on the diamond lattice. The breadth of the spectra near the base is 120 kHz, eliminating the possibility for use in a 3-site or 4-site hop model. The 3-site exchange spectra have a splitting of approximately 88 kHz and for a 4-site exchange model the splitting is around 42 kHz.[47] Apparently, a more reasonable description of the motions of the chemisorbed molecule is that it undergoes a degree of rotational diffusion as well as hopping between two sites. The two-site hop line shape is averaged further because the jumping axis itself is undergoing additional motions. In order to simulate this rotational motion, the Freed model was used which includes calculations for anisotropic rotational diffusion ($R_{\parallel}$ and $R_{\perp}$). The parallel component of the rotational diffusion is coincident with the jump axis. Rotation about the perpendicular axis may be rationalized based on the averaging of the ($3\cos^2\theta - 1$) term. Since the $\cos\theta$ is a squared term, averaging from 0° to 90° is indistinguishable from that of 0° to 180°. Overall rotation of the coupling agent is improbable because the coupling agent is bound to the surface, however, isomerization corresponding to the amino group of DABS rotating between an extended state to one bent (i.e. with gauche conformations) is possible. This is somewhat slower than the rotational diffusion about the main axis, but of a similar order of magnitude chemisorbed. The low temperature line shapes for the treated surfaces are very similar to the line shape of chemisorbed DABS reacted with BMI. It appears that as the temperature is reduced significantly, the DABS loses some of its motional freedom and no longer appears to undergo complete rotation. The motion, as indicated by the deuterium line shape, is very similar to that of chemisorbed DABS bound to a polymer matrix. The spectra are consistent with a chemisorbed DABS molecule to jumping between sites on the tetrahedral lattice with an unequal population distribution between the sites.

The motions of the surface bound DABS are faster than those considered to be in the intermediate regime. It is reasonable to expect that the DABS bound only at one end of the molecule would experience faster motions than when the DABS is reacted at both ends. The spectra of the surface bound DABS were not sensitive to the waiting period between pulses, contrary to the spectra of the DABS after reaction with BMI which did exhibit distortions. This distortion in line shape is indicative that the motions of the DABS chemisorbed on the surface and reacted with BMI occur in the intermediate regime.

For deuterium NMR line shapes, slow or ultra-slow motions are classified by $\Delta\upsilon_q \tau_c >> 1$ where $\Delta\upsilon_q$ is the quadrupole splitting and τ_c is the correlation time. For an aliphatic deuteron where the quadrupole coupling constant is 165 kHz, the splitting for a static pattern is 124 kHz. This means slow motions are those with a correlation time $> 10^{-5}$ seconds. Fast motions are those with $\Delta\upsilon_q \tau_c <<$ 1, or $\tau_c \leq 10^{-7}$ seconds. In the intermediate regime, $\Delta\upsilon_q \tau_c \approx 1$ or $10^{-5} \geq \tau_c \geq 10^{-6}$ seconds, large differences are seen between the solid-echo and single pulse deuterium line shapes. When the waiting time between pulses, τ, is comparable with the motional correlation time, the quadrupole echo line shapes are distorted and the intensity of the echo reduced significantly.[48] The loss of signal intensity can be minimized by use of shorter delay times. In the intermediate exchange regime, the apparent T_2

becomes comparable to τ and the magnetization is not completely refocussed by the second pulse. A loss in signal intensity is the result, and if the T_2 is anisotropic or orientationally dependent, distortions in the line shape results. This effect is most severe for motions that are described by a single correlation time. For more complicated systems which have a distribution of correlation times or a range of motions this effect is not as severe.[49] If intensity losses are not observed, the motions could still be in the intermediate regime but a distribution of correlation times may mask the effect.[50] Different models of motion can be discriminated by taking into account these distortions.

The model for the motions of DABS reacted to BMI describes the τ distortions well. This gives further credence to the proposed model for motion that a single jump rate is adequate to describe this system. DABS in this model composite system is bound to the surface and to the BMI polymer. Because the two ends of the molecule are held somewhat, it is analogous to polymer molecules in the solid state. One motional model which is consistent with this is Helfand type 2 motion.[51] Type 2 motions were categorized as those motions in polymers in which one of the tails undergoes a slight translation with respect to the other end. Examples of this motion are pair gauche *production* (ttt ↔ $g^{\pm}tg^{\pm}$) and gauche migration ($g^{\pm}tt$ ↔ $ttg^{\pm}$).

Molecular modelling of Helfand-type transitions on a simple molecule, $SiH_3(CH_2)_4NH_2$, was conducted using Quanta.[52] The minimum energy for each state was found and a Boltzmann distribution at room temperature was calculated to be: ttt ↔ $g^{+}t\ g^{+}$, 0.6 to 0.4; ttt ↔ $g^{-}\ t\ g^{-}$, 0.76 to 0.24; and ttg^{+} ↔ $g^{+}tt$, 0.7 to 0.3. Therefore, it is reasonable to expect that the different sites of the diamond lattice model for our more complicated system will have different occupational probabilities based on the conformation of the molecule. These values for conformational probabilities are very similar to those suggested from our spectral simulations.

Isomerization about a single bond in a polymer requires a large scale reorientation of the rest of the molecule. This large scale reorientation is improbable for DABS which is bound both to the surface and in a polymer matrix. Motions where the two ends of the chain remain stationary throughout the transition were categorized by Helfand as type 1.[51] Examples of this are the crankshaft motions and diamond lattice skeletal motions.[53] These types of motions are considered extremely rare because of the large rotational barriers that must be overcome.[51] The calculated deuterium line shapes of both of these types of motions are considerably different than those seen in this work. Helfand type 3 motions are described as a single isomerization about the center bond or the end bond (ttt ↔ ttg).[51] When these motions are simulated they give line shapes analogous to those found in this study, however this type of motion is unlikely.

Several groups have reported results utilizing ^2H NMR to study isomerizations in polymer chains.[47,54-56] The manner in which the motions are modelled varies from study to study. Jelinski *et al.*[54] calculated the line shapes for motions in poly(butylene terephthalate) by assuming a two-site hop between equally populated sites separated by 103°. The dynamics in this system were stated to be consistent with a Helfand-type motion. Huang *et al.*[47] studied polymethylene chains of glycolipid bilayers. They used a model with trans-gauche isomerizations, a two-site hop with tetrahedral jumps and varying occupational probabilities. Ebelhauser and Spiess[55] studied a polymer lipid membrane selectively deuterated in three sites. All of the spectra were simulated using a six-site jump model. Increasing temperature had the affect of not only increasing jump rates between sites, but also increasing the number of conformations accessible. At low temperatures, the model consisted of mainly a two-site exchange, but as temperature increased, all six sites were occupied reflecting the increased motional freedom. They obtained the best fit of experimental spectra by using a small distribution of jump rates and populations. Recent publications by English and coworkers[56] reported results on crystalline and amorphous nylon 66 labelled in several sites. They did not describe the motions as discrete jumps between sites with rates of hopping increasing with temperature. Rather, their model assumed uni-axial librational motion about the tetrahedral C-C axis at a rate of 10^{11} Hz. The angular amplitude increased with increasing temperature and was calculated with a Gaussian distribution of angles.

The line shapes in the works mentioned above all look qualitatively similar. In contrast to the poly(butylene terephthalate) and polymethylene chain work, the coupling agents, alone on the surface may undergo conformational changes about single bonds. This is because they are short enough that moving the "rest" of the chain is not prohibited. This less-hindered rotational motion of the coupling agents about various bonds is more appropriated approximated by the continuous diffusion model used here. However, because some of the surface-bound coupling agents are in more restricted environments, inclusion of another, more restricted motion is appropriate. We have chosen the two-site jump because it is the simplest one consistent with these types of lineshapes observed. The notion of fast angularly restricted motions is inconsistent with our data which has a distinct lineshape dependence on the quadrupole echo time--indicative of motions in the intermediate range. For the present case, we believe we have interpreted the experimental spectra in terms of the type of motion and occupational probabilities most appropriate for this system. It is clear that more experiments need to be performed to better characterize these important interfacial species.

Conclusions

The ^{13}C CP-MAS spectra provided evidence that the aminoalkyl coupling agent was incorporated into the polymer matrix near the interface. A model reaction between methylmaleimide and butylamine, analyzed by carbon-13 in the liquid state, showed the nature of the bonding to be the amine group adding across the double bond of the maleimide. Bismaleimide also appears to react with the aminoalkyl coupling agents in the same manner, both absorbed on the surface and in bulk.

Deuterium NMR has been used to probe the molecular motions of a coupling agent functioning in a model composite both as a treated surface and reacted with bismaleimide. For the coupling agent treated surface, two site jumps plus anisotropic rotation of the C-D bond of the coupling agent were consistent with the experimental spectra. When overcoated and reacted with a polymer, the chemisorbed coupling agents yield spectra which were consistent with gauche migrations or pair gauche production. These consist of counter rotation about the second neighbor parallel bonds and were simulated with a model for two site jumps on the tetrahedral lattice. Spectral changes with changing temperature were small. The spectral distortions that arose from varying the quadrupole echo time, τ, was accounted for in the simulated spectra. The overall anisotropic rotation of the surface-bound coupling agent is inhibited when overpolymerization occurs.

Deuterium NMR is a powerful tool for obtaining information about motions on the molecular level. With deuterium labelling, the dynamics of the interfacial material can be probed regardless of the optical clarity of the material. Thus, it is possible to probe the interface of a model composite system and describe it quantitatively based upon realistic models of molecular motion. In addition, the effect of overpolymerization of the treated surface was consistent with a change in the mechanism of motion as well.

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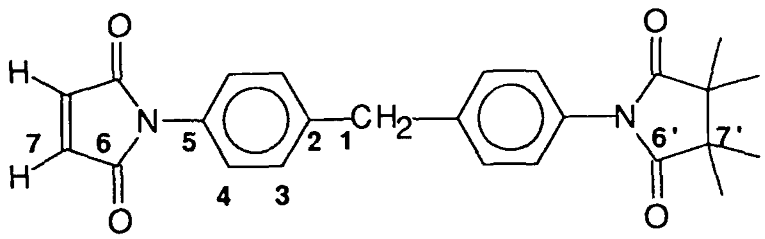
Table I. Assignments for ^{13}C solution NMR of model reaction.

	Carbon Number	Chemical Shift, ppm
A. n-Butylamine		
	1	12.5
	2	18.7
	3	34.8
	4	40.6
B. Methylmaleimide		
	1	23.5
	2	170.7
	3	134.1
C. 2-(N'-butylamino)-N-methylmaleimide		
	1	13.5
	2	19.9
	3	35.9
	4	47.0
	5	56.2
	6	31.8
	7	175.0
	8	177.7
	9	24.2

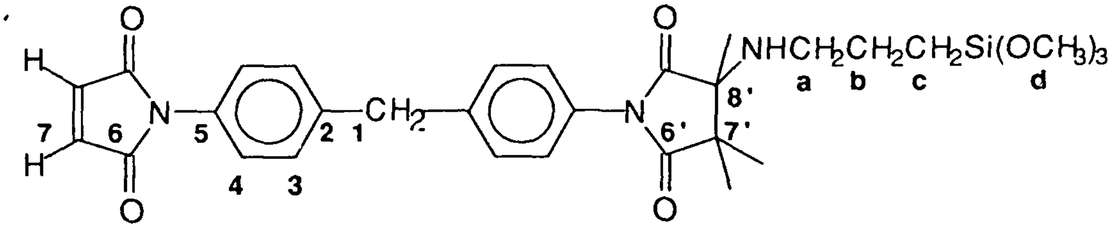
Table II. Assignments for ^{13}C NMR of bismaleimide (BMI).



Carbon Number	Chemical Shift, ppm
A. Monomer, in $CDCl_3$	
1	41.1
2	140.4
3	126.2
4,5	129.7
6	169.6
7	134.2
B. CP/MAS of Monomer	
1	39.3
2	142.4
3	126.4
4,5	129.8
6	169.1, 171.0
7	unresolved with 3 & 5
C. CP/MAS of Cured BMI	
1	41.9
2	141.1
3, 4, 5	129.4
6	169.7
7	unresolved with 3,4 & 5
6'	175.6
7'	~46

Table III. Chemical shift assignments for ^{13}C CP/MAS NMR of aminosilane coupling agents and BMI reaction.

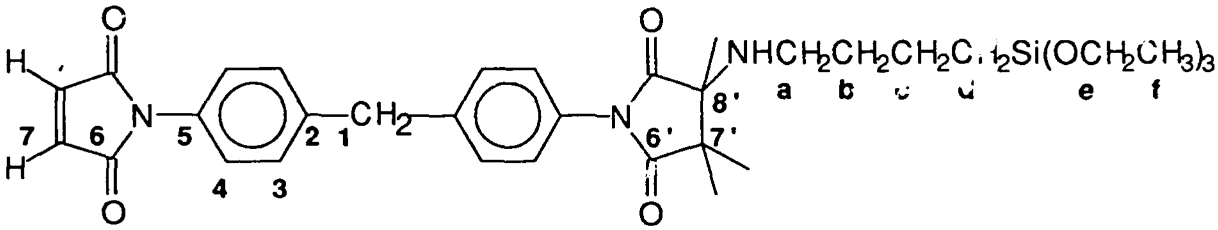
A. Product of APMS and BMI


O
H
7
H
6
N
5
4
3
2
1
CH2
N
6'
8'
7'
O
NHCH2CH2CH2Si(OCH3)3
a
b
c
d

Carbon Number	Chemical Shift, ppm
1	43.- 50
2	142.7
3, 4, 5, 7	131.2
6	171.3
6'	177.8
7'	34.5
8'	43.- 50
a	43.- 50
b	25.8
c	16.7
d	51.3

Table III (con't)

B. Product of ABES and BMI


O
H
7
6
H
O
N
5
4
3
2
1
CH₂
O
N
6'
O
8'
7'
NHCH₂CH₂CH₂CH₂Si(OCH₂CH₃)₃
a
b
c
d
e
f

Carbon Number	Chemical Shift, ppm
1	42.-48
2	141.3
3, 4, 5, 7	129.9
6	170.5
6'	175.1
7'	34
8'	42.-48
a'	42.-48
b	34
c,f	19.0
d	12.0
e	58.6

Figure Captions

Figure 1. ^{13}C NMR spectra of model reaction components (in $CDCl_3$): (A) *n*-butylamine; (B) methylmaleimide; (C) 2-(*N'*-butylamino)-*N*-methylmaleimide. The assignments are shown in the figure. The x in (C) is for the unreacted double bond in methylmaleimide.

Figure 2. ^{13}C-CP/MAS NMR spectra of coupling agent and BMI reactions: (A) product of APMS and BMI; (B) product of ABES and BMI; (C) Product of ABES and BMI with dipolar dephasing (PDP). The assignments are given in Table III.

Figure 3. ^{2}H solid echo NMR spectra (on silica grade S-17) of: (A) DABS, from 2% solution; (B) BMI over DABS, 1.5:1.0 mole ratio; (C) extra BMI polymerized over DABS, 5:1 mole ratio.

Figure 4. Temperature dependence of experimental and calculated spectra of DABS chemisorbed on silica: (A) -100 °C; (B) -60 °C; (C) 5 °C; (D) 20 °C; (E) 85 °C. See text for simulation parameters.

Figure 5. Room temperature ^{2}H solid echo NMR spectra of chemisorbed DABS with BMI reacted over it (1.5:1.0 mole ratio) - as a function of a varying delay time, τ, between pulses. Simulated spectra use a two site jump model (0.70:0.30 population) and jump rate of 1.7×10^5 sec^{-1}.

Figure 6. Temperature dependence of ^{2}H solid echo NMR spectra of DABS on silica with BMI over reacted (1.5:1.0 mole ratio). The jump rates for simulated spectra are: (A) -100 °C, 1.0×10^5 sec^{-1}; (B) -60 °C, 1.5×10^5 sec^{-1}; (C) 20 °C, 1.7×10^5 sec^{-1}; (D) 45 °C, 2.2×10^5 sec^{-1}; (E) 60 °C, 2.7×10^5 sec^{-1}; (F) 85 °C, 4.0×10^5 sec^{-1}.

Figure 7. ^{2}H solid echo NMR spectra of chemisorbed DABS with BMI reacted over it: (0.9:1.0 mole ratio of BMI to DABS) as a function of echo time, τ.

Fig 1

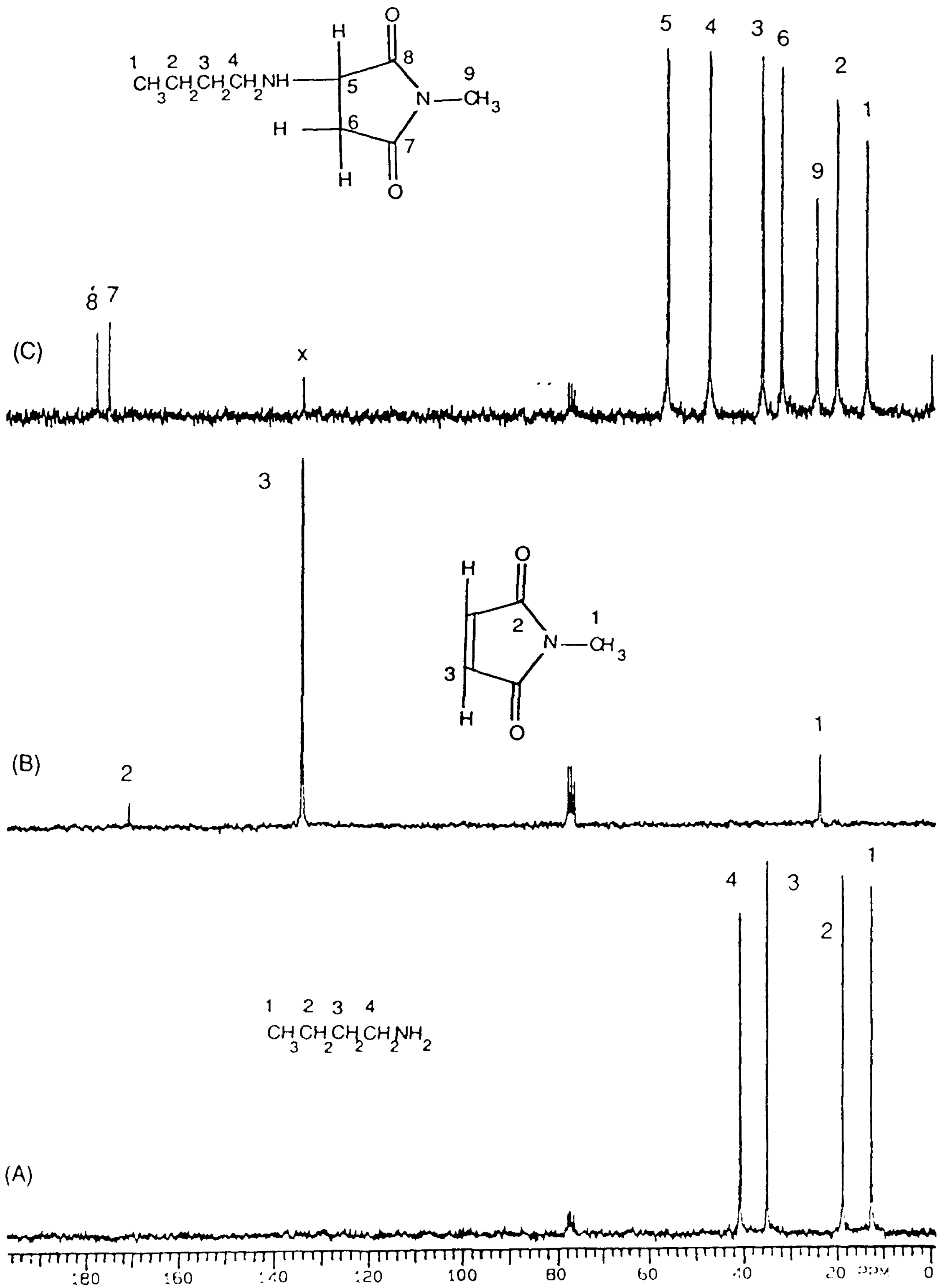


Figure 1. ^{13}C NMR spectra of model reaction components (in $CDCl_3$): (A) *n*-butylamine; (B) methylmaleimide; (C) 2-(*N*'-butylamino)-*N*-methylmaleimide. The assignments are shown in the figure. The x in (C) is for the unreacted double bond in methylmaleimide.

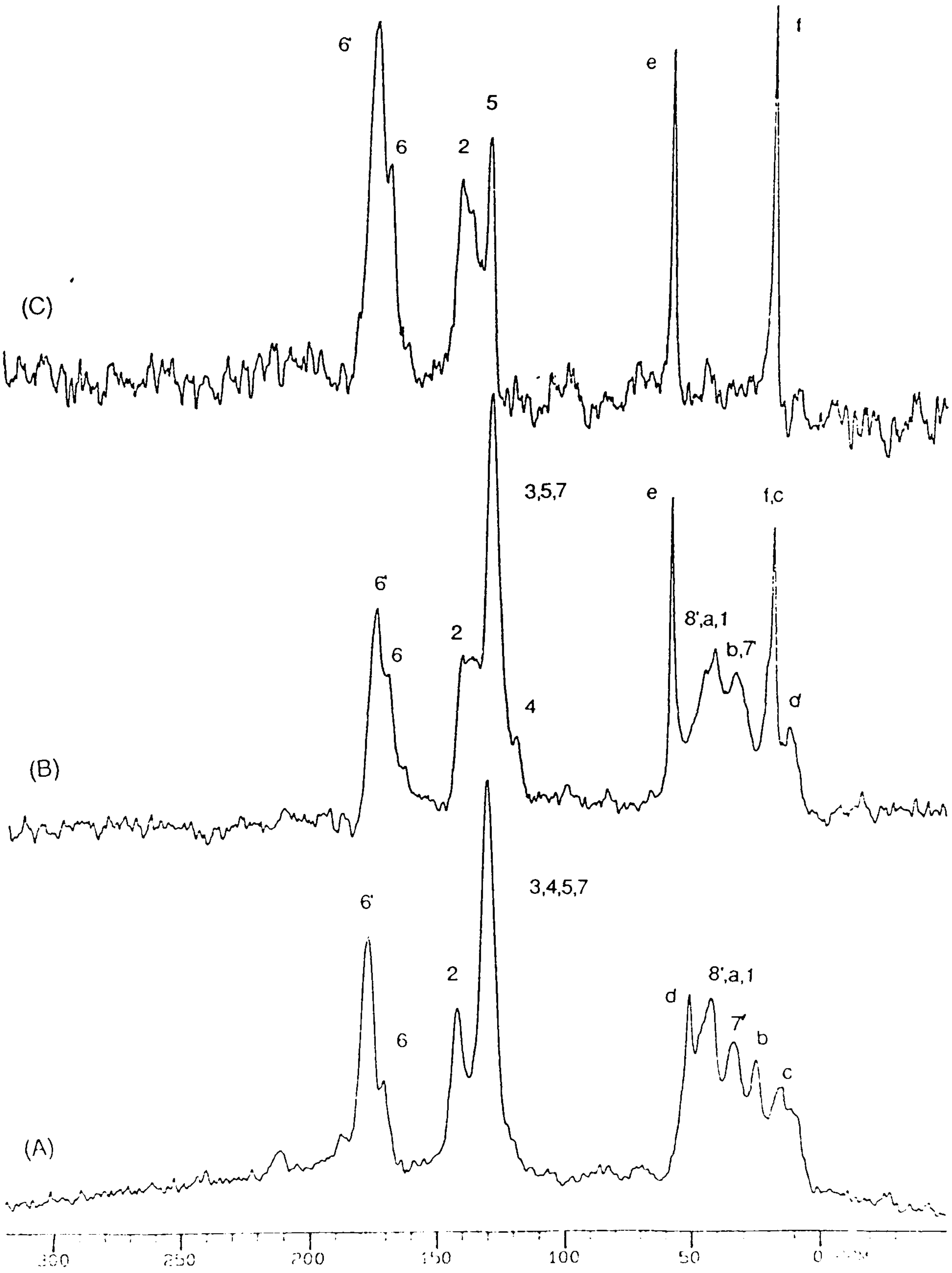


Figure 2. ^{13}C-CP/MAS NMR spectra of coupling agent and BMI reactions: (A) product of APMS and BMI; (B) product of ABES and BMI; (C) Product of ABES and BMI with dipolar dephasing (PDP). The assignments are given in Table III.

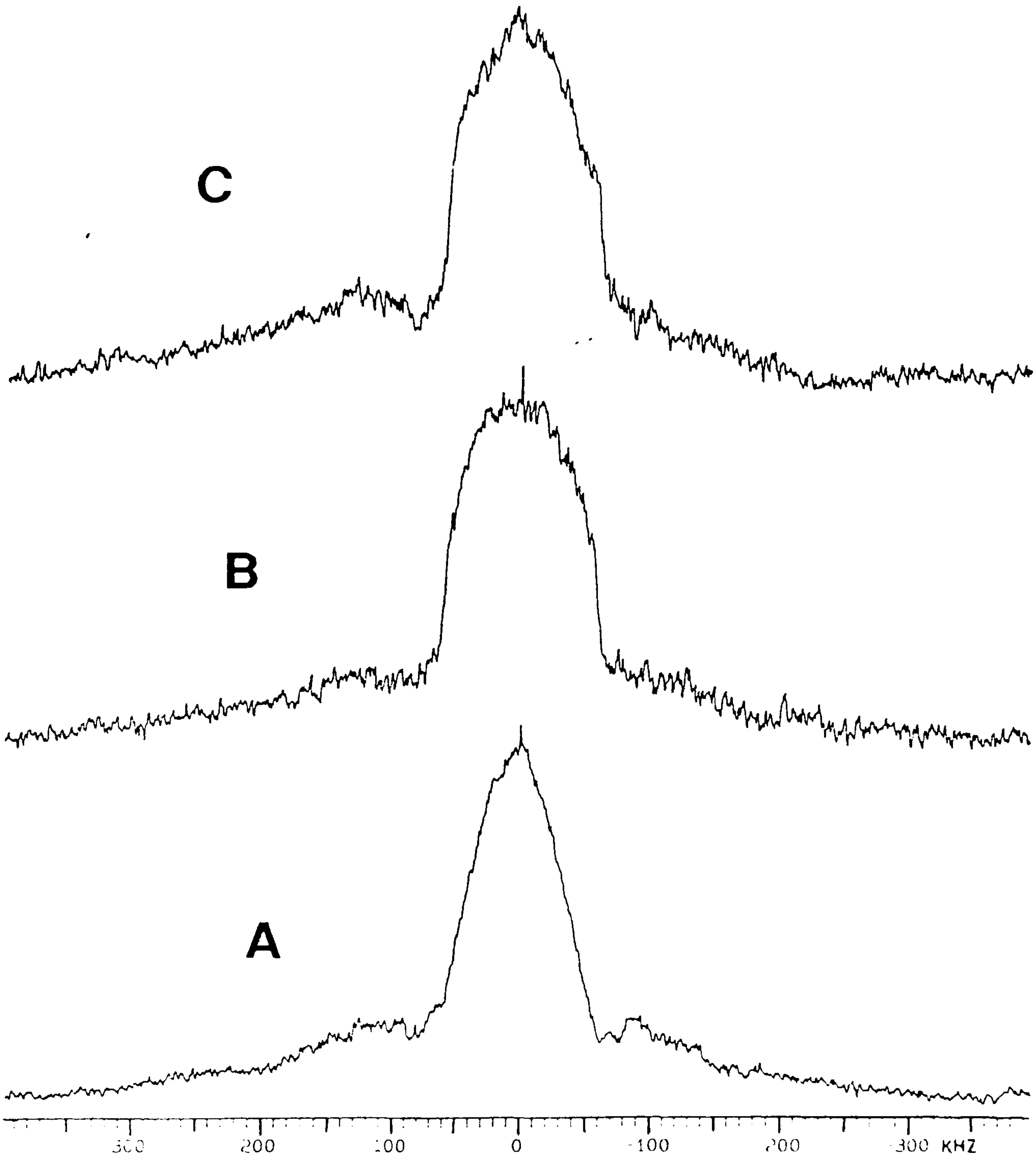


Figure 3. ^{2}H solid echo NMR spectra (on silica grade S-17) of: (A) DABS, from 2% solution; (B) BMI over DABS, 1.5:1.0 mole ratio; (C) extra BMI polymerized over DABS, 5:1 mole ratio.

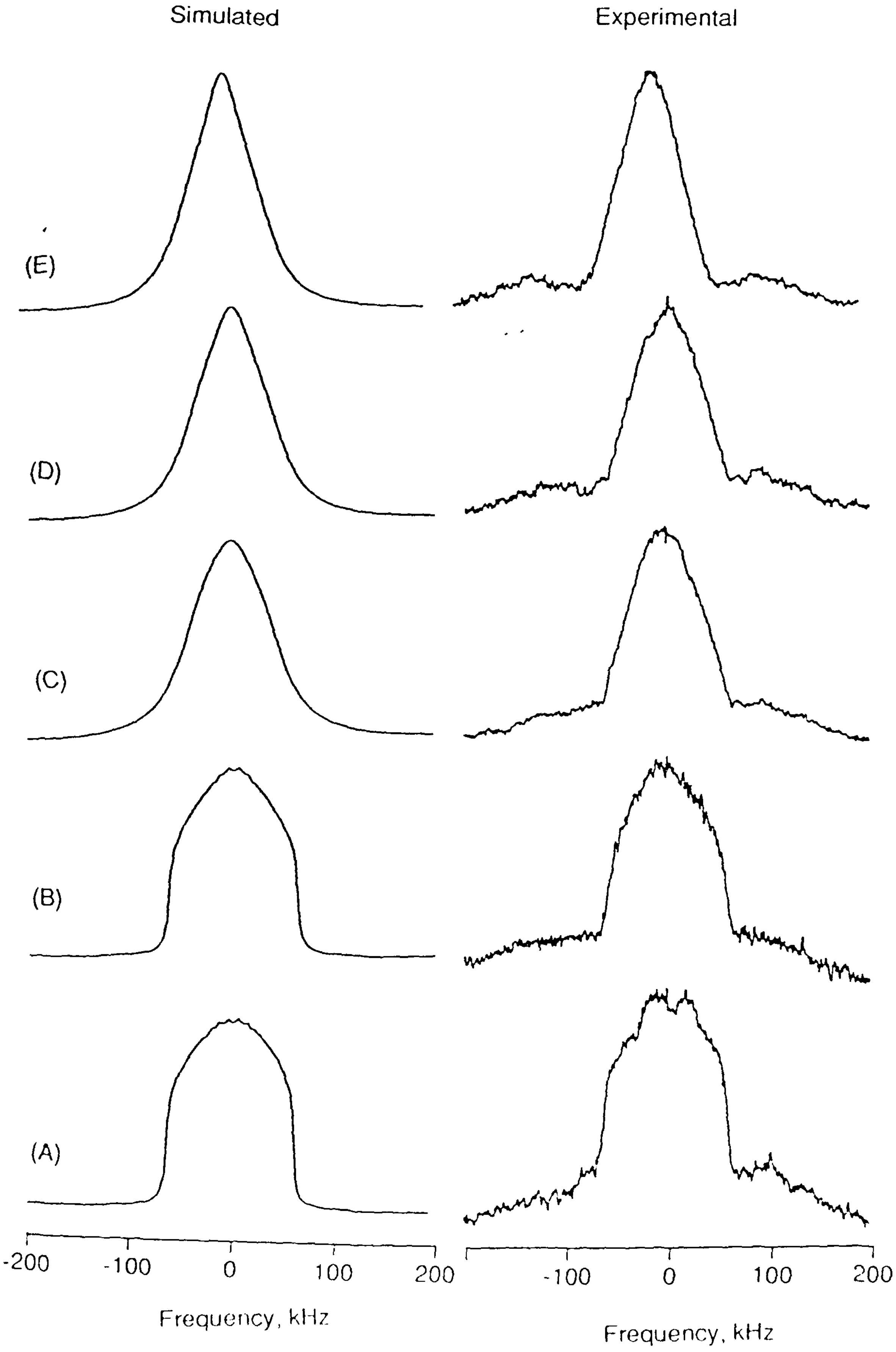


Figure 4. Temperature dependence of experimental and calculated spectra of DABS chemisorbed on silica: (A) -100 °C; (B) -60 °C; (C) 5 °C; (D) 20 °C; (E) 85 °C. See text for simulation parameters.

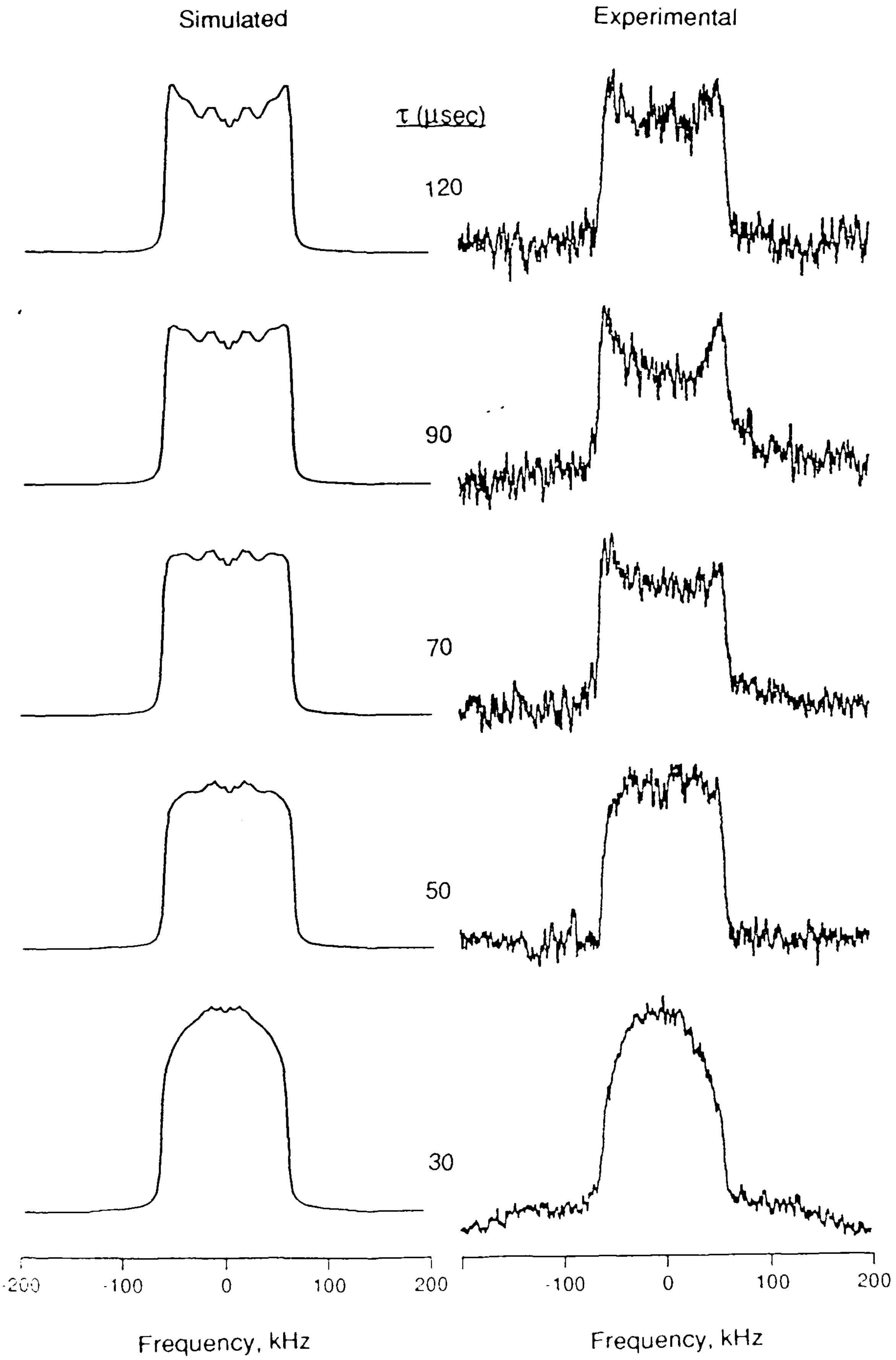


Figure 5. Room temperature ^2H solid echo NMR spectra of chemisorbed DABS with BMI reacted over it (1.5:1.0 mole ratio) - as a function of a varying delay time, τ, between pulses. Simulated spectra use a two site jump model (0.70:0.30 population) and jump rate of 1.7×10^5 sec^{-1}.

Figure 6

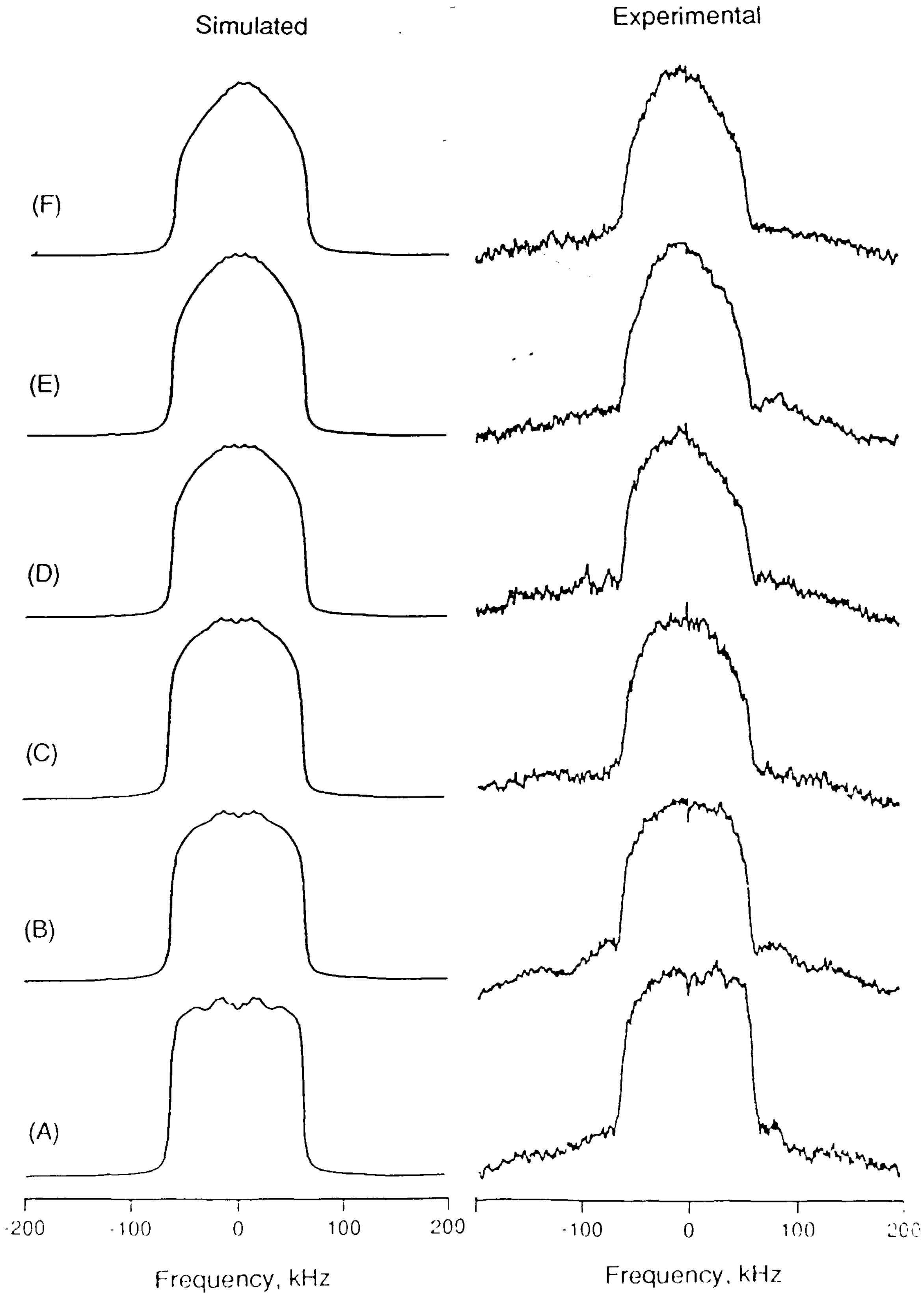


Figure 6. Temperature dependence of ^{2}H solid echo NMR spectra of DABS on silica with BMI over reacted (1.5:1.0 mole ratio). The jump rates for simulated spectra are: (A) -100 °C, 1.0 x 10^5 sec^{-1}; (B) -60 °C, 1.5 x 10^5 sec^{-1}; (C) 20 °C, 1.7 x 10^5 sec^{-1}; (D) 45 °C, 2.2 x 10^5 sec^{-1}, (E) 60 °C, 2.7 x 10^5 sec^{-1}; (F) 85 °C, 4.0 x 10^5 sec^{-1}.

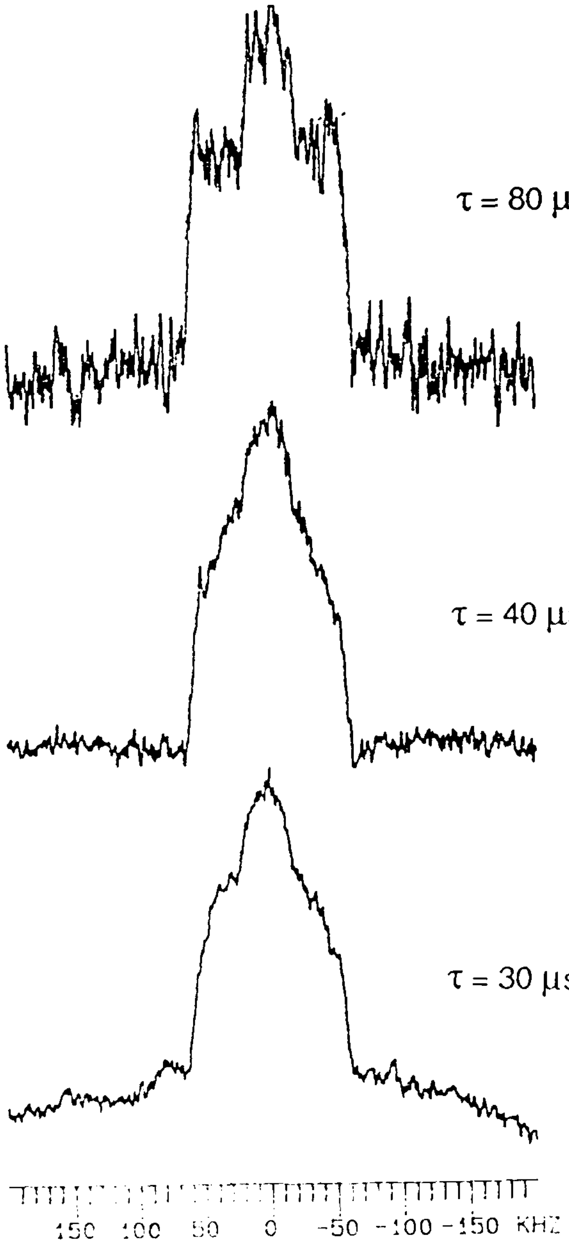


Figure 7. ^{2}H solid echo NMR spectra of chemisorbed DABS with BMI reacted over it: (0.9:1.0 mole ratio of BMI to DABS) as a function of echo time, τ.